

BD



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 125 866
B1

⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification: 03.05.89

⑥① Int. Cl.⁴: **G 02 B 5/20, G 02 B 5/22,**
G 03 C 1/84

⑦① Application number: 84303082.6

⑦② Date of filing: 08.05.84

⑤④ **Narrow band light absorbing filter.**

③⑨ Priority: 09.05.83 US 492690

④④ Date of publication of application:
21.11.84 Bulletin 84/47

④⑤ Publication of the grant of the patent:
03.05.89 Bulletin 89/18

⑥④ Designated Contracting States:
CH DE FR GB IT LI SE

⑥⑥ References cited:
EP-A-0 019 298
EP-A-0 029 412
FR-A-1 064 251
US-A-2 160 907
US-A-3 382 183
US-A-4 088 497
US-A-4 232 116

⑦③ Proprietor: MINNESOTA MINING AND
MANUFACTURING COMPANY
3M Center
Saint Paul, Minnesota 55101 (US)

⑦④ Inventor: Musser, Arlene K. Minnesota Mining
and Man. Co.
2501 Hudson Road P.O. Box 33427
St. Paul Minnesota 55133 (US)
Inventor: Koelsch, Peter M. Minnesota Mining
and Man. Co.
2501 Hudson Road P.O. Box 33427
St. Paul Minnesota 55133 (US)

⑦⑤ Representative: Bowman, Paul Alan et al
LLOYD WISE, TREGEAR & CO. Norman House
105-109 Strand
London WC2R 0AE (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 125 866 B1

Description

The present invention relates to optical filter layers for use with ultraviolet radiation (UV) and visible light imageable photosensitive media. In particular, filters are disclosed which absorb in narrow radiation bands and can be easily designed to absorb within the range of 320 to 500 nm to prevent halation in the final image.

A significant problem that has been faced in many forms of imaging technology is termed halation. This image quality diminishing phenomenon is caused by the reflection of actinic radiation which has passed through the radiation sensitive medium and struck a supporting surface in the imageable article. The reflected radiation then passes through the sensitive medium again, imaging the article in a pattern not faithful to the original exposing light pattern. This causes a reduced faithfulness in the final image.

One traditional way of reducing halation is to provide a radiation-absorbing characteristic in the supporting surface. Dye layers, carbon black layers and the like have often been used for this purpose. The use of such radiation-absorbing, anti-halation layers means that the imageable article and often the imaged article will have the color of the radiation-absorbing material of the support surface. Bleachable dyes or strippable layers are often used to allow that undesirable color contribution to be removed. That approach requires considerable manual labor and design expertise to work even moderately well and increases the cost of manufacturing the film by adding layers and coating steps.

It is generally known that ultraviolet (UV) radiation and near ultraviolet (near UV) radiation tend to be the most capable ranges of radiation with respect to halation. The use of titania-filled or coated substrates tends to greatly reduce that problem. Titania provides a clean white background and effectively absorbs much of the radiation below 380 nm. The use of titania still does not solve the problem of near UV halation (i.e., radiation between 390—480). That problem is significant in the reproduction of visible images.

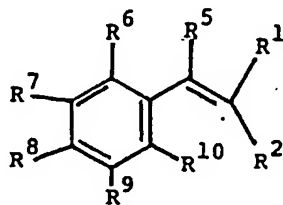
FR—A—1064251 discloses rigid and flexible materials for protecting products e.g. merchandise from the harmful effects of the sun's rays. The materials comprise a synthetic resin and dye. Suitable resins include phenol-formaldehyde resins and suitable dyes include benzylidenes.

US—A—4332116 discloses ultraviolet radiation sensitive photographic materials have a yellow filter dye e.g. a benzylidene coated over the silver halide emulsion.

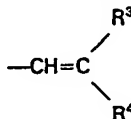
EP—A—0 029 412 discloses a class of benzylidene dyes suitable for use as antihalation and filter dyes in photographic materials.

It has been found that phenol-formaldehyde resins (both novolaks and resoles) shift the wavelength of maximum radiation absorbance of benzylidene and naphthalimide dyes. Numerous other resins have been tried with these dyes and many other dyes have been tried with phenol-formaldehyde resins, but to date only those unique combinations evidence a significant wavelength shift.

Therefore according to the present invention there is provided an optical transmission filter absorbing radiation between 320 and 500 nm comprising a phenol-formaldehyde resin binder and at least one yellow dye selected from the class of benzylidenes and naphthalimides, comprising a sufficient amount of the phenol-formaldehyde resin to cause a shift in the spectral absorbance of said dye, wherein the dye is represented by the formula:



wherein R¹ and R² are independently selected from hydrogen

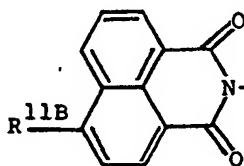


and electron-withdrawing groups, with the proviso that only one of R¹ and R² may be hydrogen, R³ and R⁴ are independently selected from electron-withdrawing groups, R⁵ is hydrogen, methyl or cyano, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are independently hydrogen, alkoxy of 1 to 4 carbon atoms, dialkyl amino (with alkyl groups of 1 to 4 carbon atoms), nitro, or amido, and one pair of adjacent groups may comprise the atoms necessary to form a fused benzene or 5- or 6-membered heterocyclic ring (comprised of only C, N, S, O and H atoms). It is highly desirable to have electron-donating groups on the aromatic ring, particularly in the positions of R⁶, R⁹ and R¹⁰ to influence the strength of absorption and the degree of colour shift. The R⁸ position appears to be the most important for this colour shift.

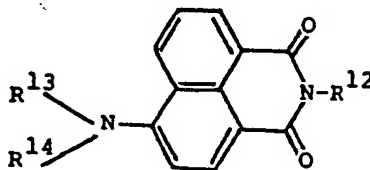
EP 0 125 866 B1

Strong electron withdrawing groups are preferred for R^1 and R^2 (and for R^3 and R^4) such as CN , $SO_2C_6H_5$, $SO_2C_xF_{2x+1}$ (where x is 1 to 8), and CO_2 -hydrocarbon, where preferably the hydrocarbon is alkyl, aryl, arylalkyl or alkylaryl (e.g., CO_2 -alkyl (1 to 4 carbon atoms in the alkyl)). With very strong electron-withdrawing groups, the remaining R^1 or R^2 group may even be a non-electron-withdrawing group such as phenyl (e.g., tolyl), although that is not preferred.

The naphthalamide dyes have a common nucleus of:



Most of these dyes can be represented by the general structural formula:



wherein R^{11} is selected from $-N$, $-O$, $-S$ or halogen, R^{12} is selected from the group consisting of alkyl of 1 to 12 carbon atoms, alkaryl of up to 12 carbon atoms, aryl of up to 10 carbon atoms and arylalkyl of up to 12 carbon atoms, and R^{13} and R^{14} are independently selected from the group consisting of hydrogen, alkyl (of 1 to 8 carbon atoms), aryl of up to 10 carbon atoms, and alkaryl of up to 12 carbon atoms (preferably tolyl).

These dyes may be conventionally mixed and dissolved with the polymeric binders and coated onto a release surface to form the filter. The filter layer may also be carried on a transparent substrate and be used in that form as a filter. After removal of the solvent, the dried film is stripped from the release surface and may be used as a filter. The phenol-formaldehyde resin may be used as 100% of the polymeric resin of the film, or may be used in smaller portions in combination with any other binder that is compatible (does not separate or cloud) with the phenol-formaldehyde resin. As smaller amounts of phenol-formaldehyde resin are used, the amount of the chromatic shift decreases. The chromatic shift in the maximum absorption of the dyes by the phenol-formaldehyde resins is always towards the red. That is, the wavelength of the λ_{max} increases with increasingly effective amounts of the phenol-formaldehyde resin. The degree of the shift may vary with individual dyes within the classes of benzylidenes and naphthalimides. Some dyes may shift only a few nm when going from 0% to 100% phenol-formaldehyde resin while others may shift 30 to 40 nm.

Any compatible resin may be used in combination with the phenol-formaldehyde resin. Amongst the preferred resins are polyvinylacetals (polyvinyl butyral and polyvinyl formal), polyethylene terephthalate, acrylic polymers and copolymers (polymethylmethacrylate), methylacrylate/methylmethacrylate copolymers, etc.), polystyrene, phenoxy resins, vinyl resins and copolymers (polyvinylidene chloride, vinyl chloride/vinyl acetate copolymers) and the like. The film should have structural integrity and should be greater than 1 mil (25.4 μm) in thickness as a single layer construction. It, of course, may be much thinner as a coating on a transparent substrate as long as it provides the desired transmission optical density. Preferably, the film is greater than 2 mils (51 μm) and usually is in the range of 5–20 mils (127–508 μm), although thicker films provide no real disadvantage. The dye containing layers may also be coated onto a transparent carrier or support layers to provide structural integrity. The dye should be present in an amount sufficient to provide a transmission optical density of at least 0.5 at the wavelength of the maximum absorption for the dye. Preferably the concentration of the dye will provide an optical density of greater than 0.8 or greater than 1.0. This may require a concentration of dye of from 0.2 to 15% by weight of the binder, depending upon the thickness of the film.

These and other aspects of the invention are shown in the following non-limiting examples:

EP 0 125 866 B1

Example 1

The two following solutions were prepared to show the chromatic shift of dyes according to the present invention:

5

	SOLUTION A (grams)	SOLUTION B (grams)	INGREDIENTS
10	9.0	0.0	modified resinox, the reaction product of Resinox RS7280 and DD1—1410 diisocyanate, as a 29.2% solids in methyl ethyl ketone solution
15	0.0	9.0	polyvinyl butyral (Butvar B-76)
20	0.30	0.30	dispersed Yellow dye 31
25	20.7	27.0	Additional methyl ethyl ketone

30 The solutions were coated onto a 2-mil (51 μ m) thick transparent polyester film with a #10 Meyer bar and dried at 190°F (88°C) for two minutes. The film produced with Solution A had an absorbance maximum at 452.8 nm, while the film from Solution B has an absorbance maximum at 424.5 nm. The shape of the absorption curves for both coatings remained approximately uniform. This enables the filter to maintain a narrow range of absorption without skewing or shifting at the toe or tail of the absorption curve. The
35 uniformity in the shape of both the peak and the width of the base was maintained.

Example 2

40 This example describes a large-scale preparation of a specific filter and its use as an effective antihalation tool. The following coating solution was prepared:

45	Dispersed Yellow Dye 31	60 g
	Butvar B-76 of Example 1	108 g
	Modified Resinox	1440 g
50	Additional MEK	1720 g

This solution was reverse roll coated onto 2-mil (51 μ m) thick photograde transparent polyester film to various optical densities, and dried at 190°F (88°C). The resulting films had absorbance maxima at 447 nm.
55 This was desired since previous experimentation had shown that a filter with this absorbance would have an optimal antihalation effect on 3M Positive Matchprint. Samples of cyan Positive Matchprint, after lamination onto a titanium dioxide-coated support, were exposed using a 5 KW diazo lamp as the UV light source through these filters, and subsequently processed with an aqueous alkaline developer. The samples exposed through the filters had substantially better image quality with little halation, especially at longer
60 exposure times. The more dense the yellow filter was made, the greater the effect on resolution and exposure latitude became.

Example 3

Each of the following dyes were used in these Examples. Five separate coating solutions were
65 prepared for each dye. The coating solutions each consisted of dye, the modified Resinox of Example 1 and

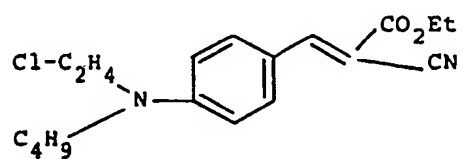
EP 0 125 866 B1

polyvinyl butyral. The composition of the individual solutions was as follows in weight percent of the dry film:

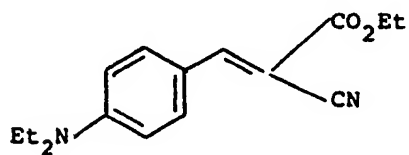
	SOLUTION	DYE	RESINOX	POLYVINYLBUTYRAL
5	A	10	90	0
10	B	10	72	18
	C	10	45	45
	D	10	18	72
15	E	10	0	90

The dyes used in the Examples had the structural formulae:

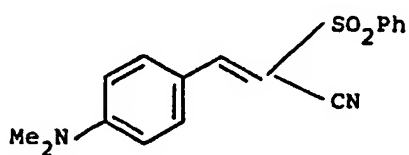
3.



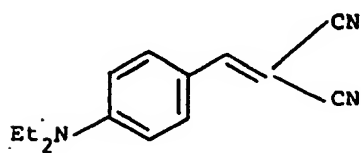
4.



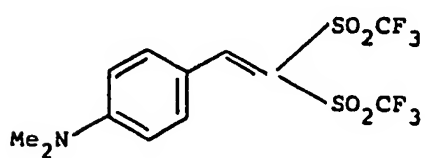
5.



6.

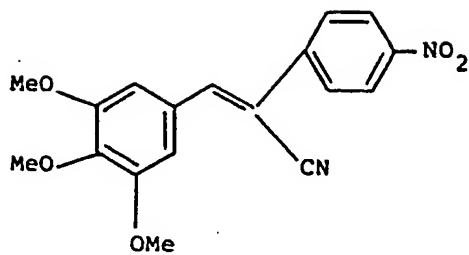


7.

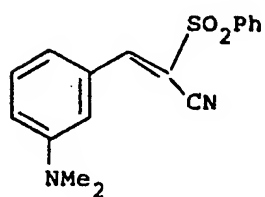


EP 0 125 866 B1

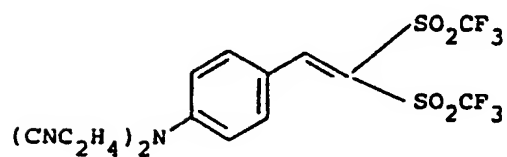
8.



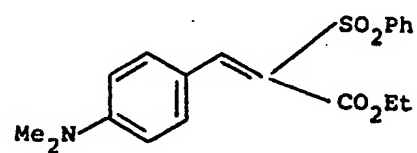
9.



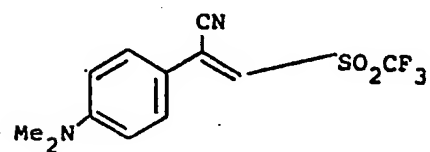
10.



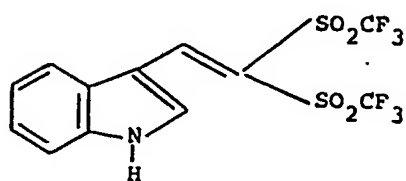
11.



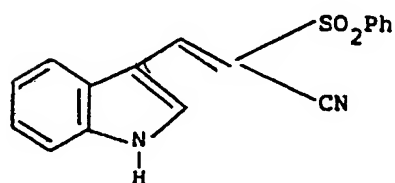
12.



13.

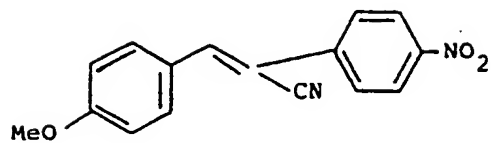


14.

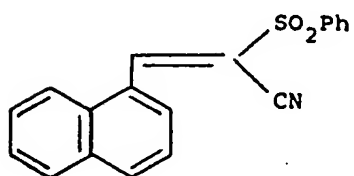


EP 0 125 866 B1

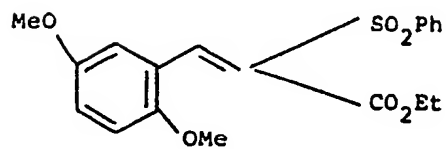
15.



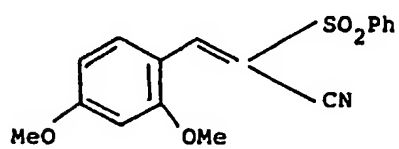
16.



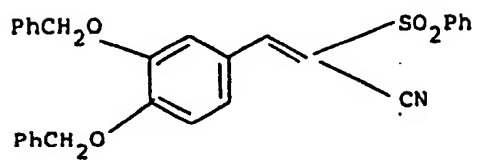
17.



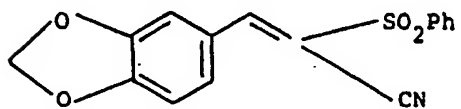
18.



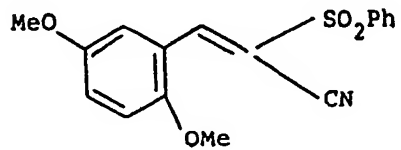
19.



20.

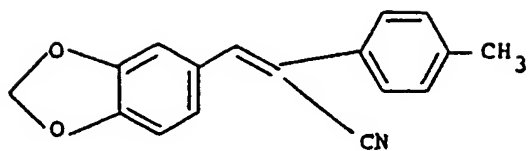


21.

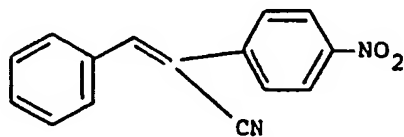


EP 0 125 866 B1

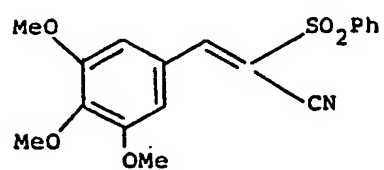
22.



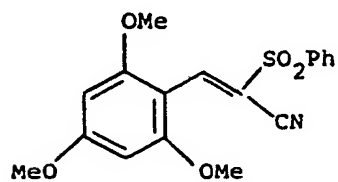
23.



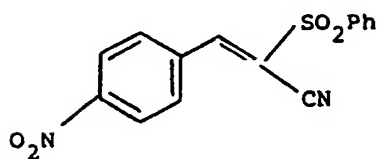
24.



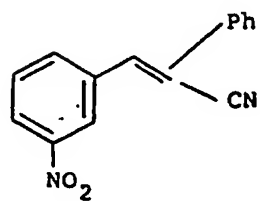
25.



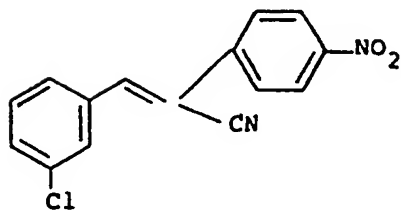
26.



27.

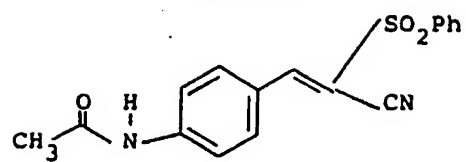


28.

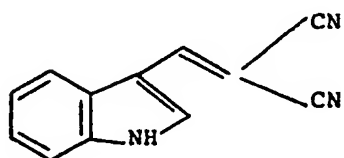


EP 0 125 866 B1

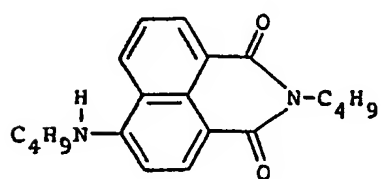
29.



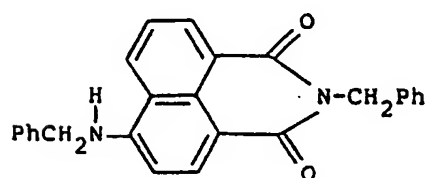
30.



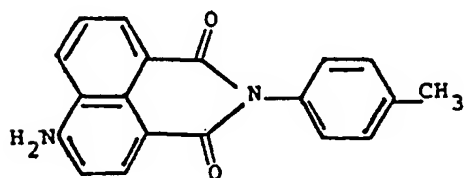
31.



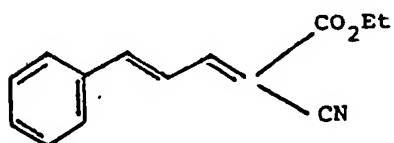
32.



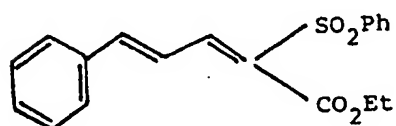
33.



34.

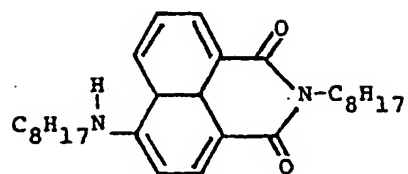


35.

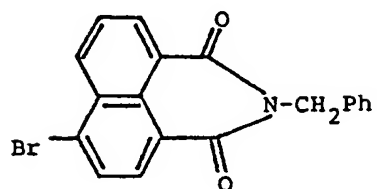


EP 0 125 866 B1

36.



37.



After coating and drying of these solutions onto a 2-mil (51 μ m) transparent polyester substrate, the following data were obtained:

EP 0 125 866 B1

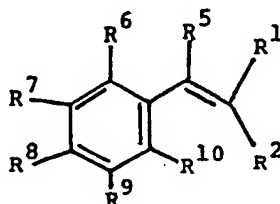
DYE	SOLUTION A			SOLUTION B			SOLUTION C			SOLUTION D			SOLUTION E		
	λ_{max}	A	$\Delta W\%$	λ_{max}	A	$\Delta W\%$	λ_{max}	A	$\Delta W\%$	λ_{max}	A	$\Delta W\%$	λ_{max}	A	$\Delta W\%$
3	452.8	2.6	64	448.2	2.3	64	438.0	2.1	66	428.0	2.6	66	424.5	1.1	62
4	454.0	2.3	57	449.0	2.27	58	440.3	3.16	58	431.7	2.6	58	424.1	1.9	58
5	449.5	2.36	56	444.0	2.55	56	436.5	2.16	56	428.6	2.04	56	421.3	2.65	60
6	460.5	2.23	73	451.9	2.05	69	445.8	2.7	70	439.4	2.63	58	436.3	2.62	65
7	462.5	1.95	74	460.8	1.48	68	457.3	1.73	63	453.1	2.71	52	448.9	1.68	61
8	378.1	.80	110	379.0	1.98	104	377.8	.80	102	376.2	.97	96	376.3	.86	94
9	<320			<320			<320			<320			<320		
10	440.3	1.24	54	439.1	1.22	53	437.2	1.42	58	434.1	1.05	62	429.8	2.23	63
11	361.8	1.68	62	357.4	2.14	52	350.0	2.92	52	340.2	1.16	53	335.5	2.64	48
12	492.5	1.13	94	488.2	1.07	88	476.5	1.27	88	465.0	2.16	82	459.4	1.41	78
13	411.0	.77	66	410.1	.77	64	408.5	1.62	60	405.6	2.06	58	402.5	1.75	56
14	398.4	.76	70	393.4	.74	70	389.1	.85	68	384.4	.71	65	383.8	.72	64
15	382.0	1.30	82	381.2	2.44	82	375.8	1.18	80	373.3	1.66	76	370.9	2.24	70
16	383.8	.50	86	379.6	.50	82	375.0	.52	84	369.2	1.04	74	368.1	.54	72
17	372.4	.41	84	369.0	.34	82	368.0	.43	82	361.8	.26	80	362.9	.47	70
18	385.6	1.00	64	382.9	.90	62	377.4	1.05	60	372.7	1.66	55	369.7	2.27	53
19	375.0	.58	82	372.4	.61	78	368.8	.64	77	366.3	1.16	70	364.1	.88	74

EP 0 125 866 B1

DYE	SOLUTION A			SOLUTION B			SOLUTION C			SOLUTION D			SOLUTION E		
	λ max	A	$\Delta W\%$	λ max	A	$\Delta W\%$	λ max	A	$\Delta W\%$	λ max	A	$\Delta W\%$	λ max	A	$\Delta W\%$
20	380.8	.78	73	377.2	.82	71	372.3	.91	66	367.8	1.31	60	365.8	2.14	59
21	416.5	.37	94	415.2	.42	90	410.2	.34	90	406.0	.47	84	402.9	.49	84
22	360.4	.93	75	359.2	1.29	73	356.8	1.09	70	354.4	1.65	66	350.0	2.13	64
23	350.0	1.21	112	342.9	1.15	100	340.8	2.3	94	337.6	1.75	94	336.3	3.26	90
24	362.1	.78	90	359.0	.68	90	357.2	.65	90	355.5	.68	88	353.9	.63	88
25	379.3	1.16	68	373.7	1.12	69	367.1	1.01	69	361.2	1.75	66	357.9	2.09	64
26	<320			<320			<320			<320			<320		
27	<320			<320			<320			<320			<320		
28	337.2	.97		330.9	.95		<320			<320			<320		
29	355.7	1.09	78	350.0	.55	84	350.0	.68	77	350.0	1.46	70	350.0	1.88	70
30	400.8	.69	72	397.5	1.15	76	392.9	1.70	68	388.2	1.85	66	386.8	1.69	64
31	453.6	.51	76	450.4	.53	78	444.6	.96	77	438.5	.68	78	431.0	.57	75
32	447.7	.39	66	446.5	.43	68	441.5	.40	68	433.8	.65	70	427.0	.40	69
33	437.1	.55	74	436.6	.47	80	435.0	.74	78	426.9	.45	78	425.4	.67	78
34	360.9	2.8	84	355.0	1.19	78	350.0	2.17	73	348.0	3.4		344.6	3.6	
35	350.0	.66	78	350.0	.68	78	350.0	1.28	72	338.4	.75		337.1	1.56	72
36	451.8	.32	66	451.8	.30	65	443.4	.41	66	435.5	.45	69	431.1	.41	68
37	448.2	.28	70	444.9	.36	70	439.9	.38	72	433.8	.36	71	429.4	.23	72

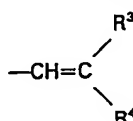
Claims

1. An optical transmission filter absorbing radiation between 320 and 500 nm comprising a phenol-formaldehyde resin binder and at least one yellow dye selected from the class of benzylidenes and naphthalamides, comprising a sufficient amount of the phenol-formaldehyde resin to cause a shift in the spectral absorbance of said dye, wherein the dye is represented by the formula:



in which:

R¹ and R² independently represent hydrogen, an electron-withdrawing group or



with the proviso that no more than one of R¹ and R² are hydrogen,

R³ and R⁴ independently represent electron-withdrawing groups,

R⁵ represents hydrogen, methyl or cyano, and

R⁶, R⁷, R⁸, R⁹ and R¹⁰ independently represent hydrogen, alkoxy of 1 to 4 carbon atoms, dialkyl amino in which the alkyl groups contain 1 to 4 carbon atoms, nitro, or amido, or one pair of groups adjacent on the benzene ring may comprise the atoms necessary to form a fused benzene ring or 5- or 6-membered heterocyclic ring comprised of only C, S, N and O ring atoms.

2. A filter as claimed in Claim 1 characterised in that at least one of R⁶, R⁸ and R¹⁰ are electron-donating groups.

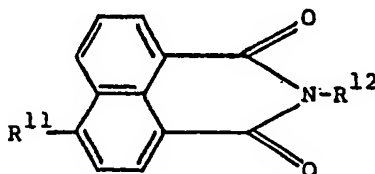
3. A filter as claimed in Claim 1 or Claim 2 characterised in that R¹ and R² are both strong electron-withdrawing groups selected from CN, CO₂R in which R is a hydrocarbon group of 1 to 12 carbon atoms, SO₂C₆H₅ and SO₂C_xF_{2x+1} in which x is 1 to 8.

4. A filter as claimed in any preceding claim characterised in that R⁸ comprises a dialkyl amino.

5. A filter as claimed in any preceding claim characterised in that at least one of R¹ and R² is cyano and the other is an electron-withdrawing group.

6. A filter as claimed in any preceding claim characterised in that the phenol-formaldehyde resin comprises from 20 to 100% by weight of the binder.

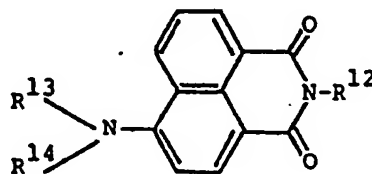
7. A filter as claimed in Claim 1 characterised in that the nucleus of said at least one dye is represented by either of the formulae:



in which:

R¹¹ represents halogen and

R¹² represents an alkyl groups of 1 to 12 carbon atoms or alkaryl groups of 1 to 12 carbon atoms, an aryl groups of up to 10 carbon atoms, or an arylalkyl group of up to 12 carbon atoms, or



EP 0 125 866 B1

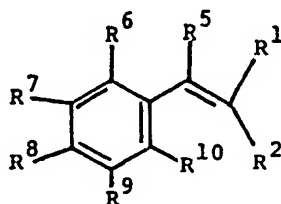
in which:

R¹² represents an alkyl group of 1 to 12 carbon atoms, an alkaryl groups of 1 to 12 carbon atoms, an aryl group of up to 10 carbon atoms, or an arylalkyl of up to 12 carbon atoms, and

R¹³ and R¹⁴ independently represent hydrogen atoms, an alkyl group of 1 to 4 carbon atoms, an aryl group of up to 10 carbon atoms or an alkaryl group of up to 12 carbon atoms.

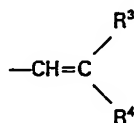
Patentansprüche

1. Strahlung zwischen 320 und 500 nm absorbierendes Lichttransmissionsfilter, umfassend ein Phenol-Formaldehyd-Harz-Bindemittel und mindestens eine gelben Farbstoff aus der Gruppe der Benzylidene und Naphthalimide mit einer ausreichenden Menge des Phenol-Formaldehyd-Harzes, um eine Verschiebung der spektralen Absorption des Farbstoffes zu verursachen, wobei der Farbstoff durch die Formel



wiedergegeben wird, in der:

R¹ und R² unabhängig voneinander Wasserstoffatome, einen Elektronen-ziehenden Rest oder den Rest der Formel



darstellen, mit der Maßgabe, daß höchstens einer der Reste R¹ und R² ein Wasserstoffatom ist, R³ und R⁴ unabhängig voneinander Elektronen-ziehende Reste bedeuten,

R⁵ ein Wasserstoffatom, eine Methyl- oder Cyanogruppe darstellt und

R⁶, R⁷, R⁸, R⁹ und R¹⁰ unabhängig voneinander Wasserstoffatome, Alkoxyreste mit 1 bis 4 Kohlenstoffatomen, Dialkylaminoreste, in denen die Alkylreste 1 bis 4 Kohlenstoffatome enthalten, Nitro- oder Amidogruppen bedeuten, oder ein am Benzolring benachbartes Restepaar, die zur Erzeugung eines kondensierten Benzolringes oder eines nur aus C, S, N und O-Ringatomen bestehenden 5- oder 6-gliedrigen heterocyclischen Rings erforderlichen Atome umfassen kann.

2. Filter nach Anspruch 1, dadurch gekennzeichnet, daß mindestens einer der Reste R⁶, R⁸ und R¹⁰ ein Elektronenliefernder Rest ist.

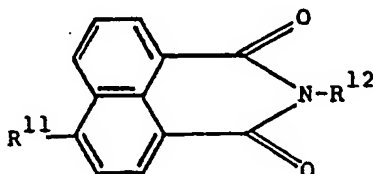
3. Filter nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß R¹ und R² beide stark Elektronen-ziehende Reste darstellen, nämlich —CN—CO₂R, wobei R einen Kohlenwasserstoffrest mit 1 bis 12 Kohlenstoffatomen bedeutet, —SO₂C₆H₅ oder SO₂C_xF_{2x+1}, wobei x einen Wert von 1 bis 8 hat.

4. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß R⁸ einen Dialkylaminorest umfaßt.

5. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß mindestens einer der Reste R¹ und R² eine Cyanogruppe und der andere ein Elektronen-ziehender Rest ist.

6. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Phenol-Formaldehyd-Harz 20 bis 100 Gew.-% des Bindemittels umfaßt.

7. Filter nach Anspruch 1, dadurch gekennzeichnet, daß der Kern des mindestens einen Farbstoffes durch eine der Formeln dargestellt wird:



in der:

R¹¹ ein Halogenatom bedeutet und

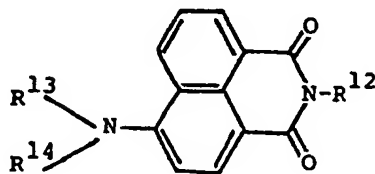
R¹² einen Alkylrest mit 1 bis 12 Kohlenstoffatomen oder einen Alkarylrest mit 1 bis 12

EP 0 125 866 B1

Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Arylalkylrest mit bis zu 12 Kohlenstoffatomen darstellt, oder

5

10



in der:

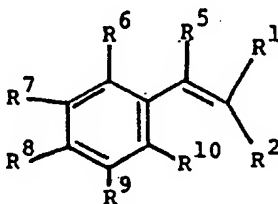
R¹² einen Alkylrest mit 1 bis 12 Kohlenstoffatomen, einen Alkylrest mit 1 bis 12 Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Arylalkylrest mit bis zu 12 Kohlenstoffatomen bedeutet, und R¹³ und R¹⁴ unabhängig voneinander Wasserstoffatome, einen Alkylrest mit 1 bis 4 Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Alkylrest mit bis zu 12 Kohlenstoffatomen bedeuten.

20 Revendications

1. Filtre de transmission optique absorbant les radiations entre 320 et 500 nm, comprenant un liant du type résine à base de phénol-formaldéhyde et au moins un colorant jaune choisi parmi la classe des benzylidènes et des naphthalimides, comprenant une quantité de résine à base de phénol-formaldéhyde suffisante pour provoquer un déplacement de l'absorption spectrale dudit colorant, dans lequel le colorant est représenté par la formule

30

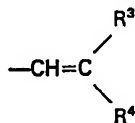
35



dans laquelle:

R¹ et R², indépendamment l'un de l'autre, représentent chacun un hydrogène, un groupe attracteur d'électrons ou

40



45

à la condition que pas plus d'un des radicaux R¹ et R² soit un hydrogène,

R³ et R⁴, indépendamment l'un de l'autre, représentent chacun un groupe attracteur d'électrons,

R⁵ représente un hydrogène ou le radical méthyle ou cyano, et

R⁶, R⁷, R⁸, R⁹ et R¹⁰, indépendamment les uns des autres, représentent chacun un hydrogène, un radical alcoxy ayant de 1 à 4 atomes de carbone, dialkylamino dans lequel les groupes alkyle contiennent de 1 à 4 atomes de carbone, nitro ou amido, ou encore deux groupes immédiatement voisins du noyau benzénique peuvent comprendre les atomes nécessaires à la formation d'un noyau benzénique condensé ou d'un noyau hétérocyclique ayant de 5 à 6 sommets et constitué uniquement d'atomes C, S, N et O.

2. Filtre selon la revendication 1, caractérisé en ce qu'au moins l'un des radicaux R⁶, R⁸ et R¹⁰ est un groupe donneur d'électrons.

3. Filtre selon la revendication 1 ou la revendication 2, caractérisé en ce que R¹ et R² sont tous les deux des groupes fortement attracteurs d'électrons choisis parmi CN, CO₂R où R est un groupe hydrocarboné ayant de 1 à 12 atomes de carbone, SO₂C₆H₅ et SO₂C_xF_{2x+1} où x vaut de 1 à 8.

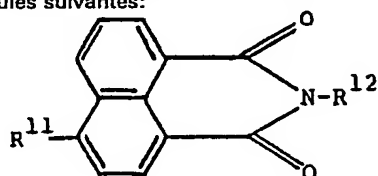
4. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce que R⁸ est un radical dialkylamino.

5. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce qu'au moins l'un des groupes R¹ et R² est le radical cyano, et l'autre est un groupe attracteur d'électrons.

6. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce que la résine à base de phénol-formaldéhyde compte pour 20 à 100% en poids du liant.

EP 0 125 866 B1

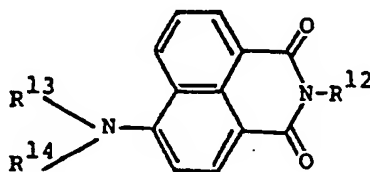
7. Filtre selon la revendication 1, caractérisé en ce que le noyau d'au moins un desdits colorants est représenté par l'une des formules suivantes:



dans laquelle

R¹¹ représente un halogène et

R¹² représente un groupe alkyle ayant de 1 à 12 atomes de carbone, ou un groupe alcaryle ayant de 1 à 12 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone ou un groupe arylalkyle ayant jusqu'à 12 atomes de carbone, ou bien



25 dans laquelle:

R¹² représente un groupe alkyle ayant de 1 à 12 atomes de carbone, un groupe alcaryle ayant de 1 à 12 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone, ou un groupe arylalkyle ayant jusqu'à 12 atomes de carbone, et

R¹³ et R¹⁴, indépendamment l'un de l'autre, représentent chacun un atome d'hydrogène, un groupe alkyle ayant de 1 à 4 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone ou un groupe alcaryle ayant jusqu'à 12 atomes de carbone.